

**DETERMINATION OF ISOTHERMAL CURVE FOR
SURFACE COMPOSITION
OF AN ALLOY IN ELECTROLYTE SOLUTION
BY THE DATA OF DOUBLE-LAYER MEASUREMENTS**

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Direct determination of the surface composition of an alloy placed into electrolyte using methods of physical analysis is rather difficult and not yet solved problem. At the same time characteristics of the double electric layer (DEL) at the boundary of A,B-alloy/solution must be very sensitive to the chemical composition of the metal plate of DEL and to the nature of surface-active metal. If certain conditions are satisfied such DEL characteristics of an alloy as differential capacity C, zero charge potential $E_q = 0$, specific surface charge q can be measured and connected with atomic fraction X_B of electropositive component B in the bulk of an alloy.

However, transition to the surface concentration X_B^ω requires the knowledge of equilibrium isothermal curve for surface composition

$X_B^\omega = \varphi(X_B)$ at 298 K.

In the frameworks of the concept of interphase layer having finite thickness (Van der Waals, Rusanov) and with account of the concentration dependence for rational activity coefficients $\ln f_A = -\beta \cdot X_B^2$, $\ln f_B = -\beta \cdot (1-X_B)^2$ for the components of an alloy in A-B system (according to Wagner) it has been shown that:

$$X_B^\omega = \frac{K X_B \exp\left(-2\beta \frac{X_B(1-X_B)(K-1)}{1+(K-1)X_B}\right)}{1 + X_B \left[K \cdot \exp\left(-2\beta \frac{X_B(1-X_B)(K-1)}{1+(K-1)X_B}\right) - 1 \right]} \quad (1)$$

Here β is a parameter of interparticle interactions in the alloy and K is a constant of solid state adsorption and $K>1$ corresponds to positive while $K<1$ - to negative adsorption of the component B. The values of K and β can be found from the experimental differential isothermal curves of the charge dq/dX_B . The form of these curves was also determined theoretically.

Alternative current double electric layer measurements were performed for the systems of Ag-Au|F, H₂O and Ag-Au|ClO₄⁻, H₂O. Poly- and mono-crystalline electrodes from Ag, Au and Ag,Au-alloys in the fluorine and perchlorate solutions were shown to be ideally polarised in a wide range of potentials including $E_{q=0}$ and they quantitatively follow DEL theory. Moreover, crystal structure and chemical composition of the surface proved to determine the values of q and the changes of specific free interphase energy $\Delta\sigma$ independently. It allows to study concentration dependencies of q and $\Delta\sigma$ with polycrystalline Ag,Au-alloys which have not been subjected to chemical polishing; this allows to exclude preliminary, before immersion into solution, enrichment of the alloy surface by gold due to selective dissolution of silver. It was found that the values of K and β do not in fact on the concentration of F⁻ and ClO₄⁻ ions and at the average they are equal to: $K = 1,46 \pm 0,12$; $\beta = 1,60 \pm 0,10$ and $K = 1,26 \pm 0,14$; $\beta = 1,21 \pm 0,13$ for KF and NaClO₄, respectively. The values of $K>1$ mean that the surface-active metal in the systems of Ag-Au|F, H₂O and Ag-Au|ClO₄⁻, H₂O is gold that can be due to the difference of hydrophilic activity for Ag and Au. Substituting K and β into (1) isothermal curve of the surface composition has been calculated; on the basis of this curve the dependencies $E_{q=0}$, q and $\Delta\sigma$ on X_{Au}^ω were obtained.

From inequality $\beta > 0$ it follows that Ag-Au alloy at 298 K is characterised by rather considerable negative deviations from Rouhlt law. Concentration dependencies f_{Ag} and f_{Au} were obtained. From these dependencies it follows that the small additions of gold have much higher effect on the change of f_{Ag} as compared with the influence of Ag on the value of f_{Au} .